Pool Rx | Spa Rx

DISINFECTION USING COPPER, SILVER AND ZINC IONS

Introduction

The purpose of this short study of literature available on the microbicidal mechanisms of copper (Cu), silver (Ag) and zinc (Zn) ions is to provide the reader with a clearer understanding and background information. It is by no means complete, and should be supplemented with new data as it becomes available. Also, the quest for information would largely be determined by the technology sector in which the reader operate e.g. a great deal of research has been done on the use on zinc in the medical field – from the treatment of colds to soar throats, and influences on the immune system. Fundamentally though, is that these ions exert microbicidal influences over a range of cellular targets, and various conditions will determine which of these influences constitute the major microbicidal effect.

Copper and silver ions have been used for centuries for disinfecting water. The early Greeks used copper and silver vessels to store water and Greek royalty stored their water in silver flagons and drank from silver goblets. The low solubility of these metals in water served as a natural controlled-release mechanism which added trace amounts of these ions to the water in the vessel. The amounts were high enough to purify the water without causing objectionable taste or health problems to the users.

Copper and silver ion disinfection of swimming pool water has several advantages over chlorine. The ions are chemically stable and do not undergo the destructive reactions that aqueous chlorine does, thus it is easier to maintain an effective residual dose. They do not form objectionable by-products such as chloramines or THM's as chlorine does. However, maintaining their concentrations in the ppb range using standard metering techniques would prove difficult to implement reproducibly and conveniently. Also, their relatively slower rates of inactivation would make it difficult to keep up with the

high bio-burden levels which occur during times of peak bather load. The problem of maintaining ppb concentrations of the ions in a convenient and reproducible manner can be solved by using electrolytic generation of the ions, or by using the ions of the metal salt solution of AquaCare.

The more recent use of copper and silver ions to inactivate microorganisms is well documented. In addition to bacteria, they also control viruses, algae, and fungi. They are as effective at the parts per billion (ppb) levels. Current EPA maximum levels for these metals are 1 ppm for copper and 50 ppb for silver. At these levels, their inactivation rates are lower than that of chlorine. Extremely small amounts of silver have significant effects on bacteria, a phenomenon referred to as oligodynamic activity. Silver has the most powerful oligodynamic activity of the metals, followed closely by copper. The oligodynamic activity of metals provides a valuable alternative to the use of systemic antibiotics and/or disinfectants in certain situations.

Mechanism of copper and silver disinfection

Researchers have performed a number of studies which have shed light on the mechanism of copper injury to bacterial cells. It was initially observed that copper-induced damage through the copper ion concentrations in the system. Laboratory experiments confirmed that levels of copper as low as 25 and 50 ppb caused 90% bacterial cell injury in 6 and 2 days respectively. Copper-injured E. coli cells were subjected to physiology studies in which oxygen uptake was monitored. It was found that the injured cells had significantly lower oxygen uptake than healthy cells and associated the damage to the respiratory chain. It can therefore be hypothesized that the damage was caused by copper binding to the sulfhydryl-groups of respiratory enzymes in the cell membrane.

A series of experiments to study the metabolism of copper-injured E. coli were also done. C-13 NMR and Gas Chromatography (GC) were used to study differences in metabolism between injured and healthy bacteria. The NMR and GC studies of metabolism were carried out on E. coli cells grown under aerobic and anaerobic

conditions, using glucose and succinate as nutrients. These studies showed inhibition of glycolysis and tricarboxylic acid activity in the copper-treated cells in comparison to healthy cells. Again, damage to cell surface enzymes by copper was implicated as the cause of reduced metabolic activity.

Studies on mice to determine the survival and virulence of chlorine and copper-injured Yersinia enterocolitica bacteria were done. It was found that fewer of the copper-damaged cells in orally- inoculated mice survived attack by low gastric pH than did the chlorine-damaged cells. The virulence of the copper-damaged cells was therefore significantly lower than the chlorine- damaged cells, which were similar in virulence to undamaged controls.

Legionella pneumophila has been shown to be killed within 6 h on exposure to a silver ion solution of 0,05 ppm. In hospitals, silver has been combined with copper ions for the control of Legionella in water systems. Evaluations have been made of the efficacy of Cu–Ag ionization in eradicating L. pneumophila from hospital water supplies. Legionella species have been shown to persist in the distribution system containing < 0,3 ppm Cu and < 0,03 ppm Ag. However, when Cu and Ag concentrations were > 0,4 ppm and > 0,04 ppm, respectively, significant decreases in Legionella occurred. Copper and silver ions have been found to be superior to thermal treatment for the removal of Legionella. Fewer sites throughout the distribution system were positive for Legionella when using the Ag and Cu ions. Fewer nosocomial cases of legionellosis were also observed when Ag/Cu ions were implemented.

In a study conducted on the copper/silver/iodine system it was found that there were two populations of bacteria in the system exposed to iodine alone; the majority of the bacteria which were inactivated by the treatment and a small population that was resistant to it. This latter population was responsible for regrowth after the iodination was stopped. The bacteria exposed to the copper and silver metal ions did not exhibit regrowth. The authors described this as being due to different modes of action of the iodine and the metal ion systems.

Three possible mechanisms have been proposed for inhibition of microorganisms by silver: interference with electron transport, binding to DNA, and interaction with the cell membrane. The formation of complexes with sulfhydryl groups can inactivate cell surface enzymes and interfere with respiration at the cell membrane.

Copper is known to attack respiratory enzymes in bacteria, presumably by binding to groups containing; sulfhydryl, amine, and carboxyl moieties. Copper is also thought to facilitate hydrolysis or nucleophilic displacement reactions in peptide chains or nucleic acids. Finally, copper is able to chelate with phosphate groups and this could result in the opening of the DNA double helices.

Although a number of studies exist which document changes in metabolism and inactivity of microorganisms which have been damaged by metal ions, there has not yet been a definitive work which links the changes caused by the metal ions on a molecular level. There is an even greater scarcity of data on changes in metabolism and infectivity of microorganisms damaged by synergistic combinations of various metal ions.

Little is known or has been proposed about the changes occurring on the molecular level caused by metal ion combinations as well. The most probable molecular mechanism is a two- step mechanism to explain how two (or more) different chemical molecules may result in more efficient disinfection when used together or sequentially. It was proposed that attack by copper on the cell walls may make them more permeable to other charged metal ions such as silver or zinc which are normally excluded by healthy cells.

Mechanism of zinc disinfection

The health beneficial effect of zinc on humans is multi-factorial and is based on (1) direct antiviral effects of zinc ions, (2) amplification and maintenance of immunity, (3) augmentation of interferon activity and (4) a natural defense mechanism at the cell membrane level.

Our bodies cannot store zinc and modern diets are too low in zinc and as such zinc deficiency is a worldwide public health problem, therefore it is worth considering zinc supplementation as a prophylactic and therapeutic measure against flu, even the avian flu virus H5N1. A healthy immune system is essential for good health and well-being especially when viruses can put the immune system under stress.

A skin attachment model was used to determine if ZnCl2 would reverse or inhibit Salmonella attachment to a broiler's skin. Skin micrographs indicated that 25 mM and 50 mM ZnCl2 reduced Salmonella attachment by 69% and 99.9%, respectively, in the reversal experiments. In the inhibition experiments, 25 and 50 mM ZnCl2 reduced firmly attached cells by 82 and 91%, respectively. Reduction of Salmonella may be attributed, in part, to the bactericidal activity of ZnCl2 in addition to bacterial cell detachment.

Despite limited evidence of efficacy from well-designed clinical trials, complementary and alternative natural products such as Echinacea, feverfew leaf, ascorbic acid, garlic, and zinc salts continue to gain popularity in the self-care approach to treating colds. One of the most controversial and popular natural remedies for the common cold is zinc salts. Zinc lozenges and lollipops are widely available in drug stores and supermarkets and are heavily promoted to the public.

At concentrations of 0,1 mM/l, zinc is able to inhibit in vitro replication of several viruses known to cause the common cold. However, zinc's exact mode of action in vivo is unknown. Several mechanisms have been postulated and are reviewed. Proposed mechanisms by which zinc may exert its therapeutic effect include inhibiting viral capsid protein production, inducing the production of gamma interferon, and stabilizing and protecting plasma membranes against lysis by cytotoxic agents. Another suggested mechanism involves zinc inhibiting rhino viral interaction with intercellular adhesion molecules - the site where the virus initially binds to epithelial cells. Some have also proposed that zinc may interfere with the release of histamine and other inflammatory mediators from mast cell granules. Still others have noted that zinc does

have immune-enhancing properties, at least at the deficiency end of the nutritional spectrum. Individuals who are zinc-deficient, such as children from economically disadvantaged populations, adolescents with low dietary intake of zinc, and adults with subclinical zinc deficiency, may benefit from zinc supplementation through an enhancement of cellular immunity. The properties of the bactericidal action of silver as affected by inorganic salts and ion chelators suggest that when silver ions come into contact with bacterial cells, the silver ions are transferred into the cells, and the subsequent generation of reactive oxygen species in the cells are involved in the bactericidal activity of the silver ions.

The bactericidal activity of silver ion has been known since ancient times, and its spectrum is rather broad. Silver ion reacts with the thiol-group in vital enzymes and inactivates them or interacts with DNA, resulting in marked enhancement of pyrimidine dimerization by photodynamic reaction and possible prevention of DNA replication. Structural changes in the cell envelope and the presence of some small electron-dense granules formed with silver and sulfur have also been demonstrated in bacterial cells.

It is proposed that two possible successive processes may be involved in the action of silver. First, bacterial cells that make contact with silver take up silver ions, which inhibit several functions in the cell and consequently damage the cells. The second is the generation of reactive oxygen species, which are produced possibly through the inhibition of a respiratory enzyme(s) by silver ions and attack the cell itself.

It is hoped that this information provides a guide into the possible mechanisms of microbicidal efficacy of copper, silver and zinc ions.